# Exchange Interaction in Polynuclear Complexes. Part 3.[1] Experimental Study and Theoretical Interpretation of the Antiferromagnetic Coupling in Di-$\mu$-oxo-octaoxodichromate(III); Comparison with Tri-$\mu$-chloro-hexachlorodichromate(III)

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The temperature dependence of the magnetic susceptibility of the new material $Cr_2Te_4O_{11}$ has been studied in the range 4.2—300 K. The compound contains the binuclear anion $[Cr_2O_{12}]^{14-}$ as isolated units, resulting from sharing of an edge between two $CrO_6$ octahedra. The exchange-interaction parameter $J$ of the H.D.V.V. Hamiltonian $-J\hat{S}_A\hat{S}_B$ is equal to $-6 \pm 0.5$ cm$^{-1}$. In the framework of a previously described model for the exchange interaction and using the iterative extended-Hückel method, the antiferromagnetic contribution of the exchange interaction has been calculated. A similar calculation has been carried out for the binuclear anion $[Cr_2Cl_9]^{3-}$. Comparison of the results for both compounds shows that our model leads to the relative magnitude of the exchange interaction in cases of antiferromagnetic coupling.

THE problem of exchange interaction in polynuclear complexes and heavily doped crystals continues to produce a large number of studies. One of the aims of those working on this problem is to be able to predict, at least in a comparative way, the sign and the magnitude of the exchange interaction in a polynuclear complex according to the nature of the transition ions, the nature of the terminal and bridging ligands, and the molecular geometry, as they are revealed by the magnetic behaviour of this complex. This information cannot be obtained by considering only the Heisenberg–Dirac–Van Vleck (H.D.V.V.) phenomenological model where the exchange interaction, purely orbital in nature, is described by a formal spin–spin coupling. In order to predict the magnetic behaviour of a polynuclear system, it is necessary to know the nature (orbital and spin degeneracies) and the relative energies of the low-lying terms which may be thermally populated. Only an orbital model can eventually lead to such knowledge.

In the first two papers of this series [1] we proposed an orbital model for the exchange interaction which is based on the following four principles: (*i*) invariance with respect to a unitary transformation between the orbital-basis functions; (*ii*) validity of Heitler–London wavefunctions for the low-lying terms; (*iii*) no difference in nature between direct and indirect exchange interaction; and (*iv*) possible interpretation of the phenomenon by considering only the ground configuration, the coupling between ground and metal–metal charge-transfer configurations adding only a small second-order effect. Therefore, the wavefunctions associated with the low-lying terms are expressed in the form of sums of Slater's determinants built from the magnetic orbitals. We call magnetic orbitals the partially occupied *d* orbitals of each transition ion, delocalized over the ligands surrounding this ion. These magnetic orbitals may be determined by the molecular-orbital (m.o.) approach in each monomeric part of the polynuclear complex. The exchange Hamiltonian $H'$ is expressed as the sum of a one-electron operator $H_{AF}'$ and a two-electron operator $H_F'$. $H_{AF}'$ couples the magnetic orbitals in such a way that its eigenfunctions and eigenvalues are the m.o.s in the polynuclear complex built from these magnetic orbitals and their energies. $H_F'$ is the sum of the electronic-repulsion

$$H' = H_{AF}' + H_F' \quad (1)$$

potentials between unpaired electrons centred on two different transition ions.

Here, we only consider binuclear systems A–B in which the exchange interaction occurs between orbital singlets, well separated in energy from the first excited terms. In this case, our approach gives an orbital justification for the use of the phenomenological H.D.V.V. model. The energies of the low-lying terms may be expanded according to the increasing powers of the overlap integrals between magnetic orbitals. If we restrict ourselves to the first-order terms in these expansions, the relative energies follow the Landé interval rule. $H_{AF}'$ and $H_F'$ lead to the antiferromagnetic and ferromagnetic contributions to the exchange interaction respectively. If the H.D.V.V. Hamiltonian is defined by $-J\hat{S}_A\hat{S}_B$ where $\hat{S}_A$ and $\hat{S}_B$ are the electronic-spin operators for the transition ions located in A and B, the exchange-interaction parameter $J$ may be considered as the sum of an antiferromagnetic component $J_{AF}$ and a ferromagnetic component $J_F$. $J_{AF}$ is given by (3) where

$$J = J_{AF} + J_F \quad (2)$$

$$J_{AF} = \frac{2}{n^2}\sum_{i=1}^{n} |\Delta_i S_i| \quad (3)$$

$n$ is the number of magnetic orbitals $\phi_{Ai}$ (or $\phi_{Bi}$) around each transition ion, $S_i$ is given by (4), and $\Delta_i$ is the

$$S_i = \langle\phi_{Ai}|\phi_{Bi}\rangle \quad (4)$$

energy gap between the antibonding and bonding m.o.'s built from $\phi_{Ai}$ and $\phi_{Bi}$, calculated from the low-lying term of highest spin multiplicity. $J_F$ is given by (5) and (6).

Relations (3) and (5) were derived for $n$ varying from

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[1] Part 1, O. Kahn and B. Briat, *J.C.S. Faraday II*, **1976**, 268; part 2, p. 1441.

1 to 5. In a subsequent paper, the more general case of $N$ coupled transition ions will be considered, $N$ being any integer greater than 1, and relations for the antiferromagnetic and ferromagnetic components of the exchange interaction, valid for any $N$ and $n$, will be derived. As previously shown,[1] Hoffmann and his

$$J_F = \frac{2}{n^2} \sum_{i \in A}^{n} \sum_{j \in B}^{n} J_{ij} \qquad (5)$$

$$J_{ij} = \langle \phi_{Ai}(1)\phi_{Bj}(2) \left| \frac{1}{r_{12}} \right| \phi_{Ai}(2)\phi_{Bi}(1) \rangle \qquad (6)$$

co-workers [2] recently derived an expression for $J_{AF}$, somewhat similar to (3). Relation (5) for $J_F$ had already been obtained by many workers.

When, for symmetry reasons, all the overlap integrals $S_i$ are zero or nearly zero, $J_{AF}$ becomes negligible and the coupling is ferromagnetic. This situation occurs rather rarely. Moreover, in some cases, where a ferromagnetic coupling has been postulated from magnetic-susceptibility measurements, more careful studies should be carried out. As soon as the overlap integrals $S_i$ are not all zero, $J_{AF}$ becomes predominant. This situation is emphasized in this paper.

In Part 1 of this series our orbital model was applied to the study of binuclear complexes of $Cr^{III}$ where two octahedra share a vertex, an edge, or a trigonal face. For the first and the third types of binuclear complexes we referred to $[(H_3N)_5CrOCr(NH_3)_5]^{4+}$ and $[Cr_2Cl_9]^{3-}$. On the other hand, we did not know any binuclear complex of $Cr^{III}$ where two octahedra shared an edge. Since then, the compound $Cr_2Te_4O_{11}$ has been prepared and its crystal structure determined.[3] This compound contains the binuclear anion $[Cr_2O_{10}]^{14-}$ as isolated units. The structure of $[Cr_2O_{10}]^{14-}$ results from the sharing of an edge between two $CrO_6$ octahedra.

In this paper we study the temperature dependence of the magnetic susceptibility of $Cr_2Te_4O_{11}$ and deduce from these magnetic data the exchange-interaction parameter in $[Cr_2O_{10}]^{14-}$. Then we seek to give a theoretical interpretation of the experimental result. Finally, we compare $[Cr_2O_{10}]^{14-}$ and $[Cr_2Cl_9]^{3-}$ and show that for these two complexes it is possible to predict the order of magnitudes and the relative values of the exchange-interaction parameters.

## EXPERIMENTAL

*Determination of $J$ in* $[Cr_2O_{10}]^{14-}$.—The preparation and the $X$-ray study of $Cr_2Te_4O_{11}$ were reported by one of us.[3] The crystal structure of this compound is characterized by $[Cr_2O_{10}]^{14-}$ anions as isolated units formed by two octahedra sharing an edge and such units are connected to tellurium(IV) ions and $[Te_2O]^{6+}$ groups. The actual site symmetry of each $Cr^{III}$ ion is $C_1$ and the actual molecular symmetry of $[Cr_2O_{10}]^{14-}$ is $C_s$. Nevertheless, the geometry of $[Cr_2O_{10}]^{14-}$ is such that these symmetries are very close to $C_{2v}$ and $D_{2h}$ respectively. We notice that the intramolecular Cr–Cr distance is 3.10 Å. This value is very close to the Cr–Cr distance in $[Cr_2Cl_9]^{3-}$ (3.12 Å).

The magnetic susceptibility was determined on a polycrystalline powder by a Foner-type vibrating-sample magnetometer operating at a field strength of 17 700 G.* The independence of the susceptibility from the magnetic field strength was checked over the whole range 4.2—300 K.

$$\mu_{eff.}^2 = \frac{3kT\chi}{2N\beta^2} \qquad (7)$$

Figure 1 shows the variation between 4.2 and 77 K of the molar magnetic susceptibility $\chi$ (in cm$^3$ mol$^{-1}$) and of the effective magnetic moment per chromium(III) ion $\mu_{eff.}$ deduced from $\chi$ by the expression (7) where $3k/N\beta^2 = 7.9931$. A correction for diamagnetism, estimated at $-210 \times 10^{-6}$ cm$^3$ mol$^{-1}$, is taken into account in Figure 1. In the range 77—300 K, the magnetic susceptibility perfectly follows a Curie–Weiss law, $\chi = C/(T + \theta)$ with $C = 3.67$ cm$^3$ K mol$^{-1}$ and $\theta = 15.2$ K.

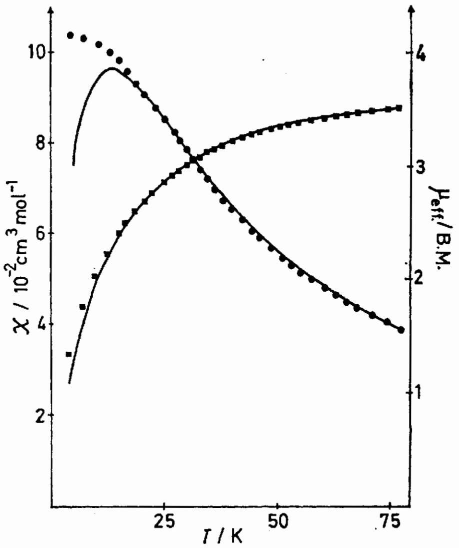

FIGURE 1 Experimental and calculated temperature dependences (for $g = 1.965$ and $J = -6$ cm$^{-1}$) of the molar magnetic susceptibility and of the effective magnetic moment per chromium(III) ion for $Cr_2Te_4O_{11}$. The experimental values are plotted for the susceptibility $\chi$ (●) and for the effective moment $\mu_{eff.}$ (■). The calculated curves are continuous lines

The parameter $g$ was determined by e.s.r. spectroscopy at 120 K. The spectrum exhibits a rather broad line of *ca.* 500 G. The $g$ value is $1.965 \pm 0.005$. This value was introduced into equation (8) giving the variation of $\chi$ with temperature in the H.D.V.V. model for the interaction between two spin quartets, where $x = -J/kT$.

$$\chi = \frac{2g^2N\beta^2}{3kT} \left( \frac{42 + 15e^{3x} + 3e^{5x}}{7 + 5e^{3x} + 3e^{5x} + e^{6x}} \right) \qquad (8)$$

Excellent agreement between the experimental data and the curve calculated from equation (8) was obtained in the range 18—300 K for $J = -6 \pm 0.5$ cm$^{-1}$. The theoretical variations of $\chi$ and $\mu_{eff.}$ are plotted in Figure 1. Below 18 K, the agreement is less satisfying. The experimental magnetic susceptibility is then greater than expected. Thus, we do not observe the maximum in $\chi$ expected from equation

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* Throughout this paper: 1 G = $10^{-4}$ T; 1 eV ≈ $1.60 \times 10^{-19}$ J.

[2] P. J Hay, J. C. Thibeault, and R. Hoffmann, *J. Amer. Chem. Soc.*, 1975, **97**, 4884.

[3] G. Meunier, B. Frit, and J. Galy, *Acta Cryst.*, 1976, **B32**, 175.

(8) at 13 ± 1 K. This disagreement probably arises from contamination of the compound by a paramagnetic monomer which may not necessarily be a chemical impurity in the sample but could result from breaking of chromium(III) pairs on the surface of the particles. A weak but significant Cr–Cr intermolecular interaction may also contribute to the magnetic behaviour observed at very low temperature.[4]

## THEORETICAL STUDY OF $J_{AF}$ IN $[Cr_2O_{10}]^{14-}$ AND COMPARISON WITH $[Cr_2Cl_9]^{3-}$

The exchange interaction in $[Cr_2O_{10}]^{14-}$ is weakly antiferromagnetic. In other words, the $J_{AF}$ component arising from $H_{AF}$ is in absolute value greater than the $J_F$ component arising from $H_F$. We want to calculate $J_{AF}$ from relation (3). For this we must be able to determine the m.o. energy levels in $[Cr_2O_{10}]^{14-}$. The number of atomic orbitals to consider does not allow use of an *ab initio* method. Such a calculation can only be carried out by a semiempirical method. We used the version of the extended-Hückel method recently employed by Hoffmann and his co-workers.[2] The diagonal Hamiltonian matrix element $H_{\mu\mu}$ is given by (9) where $q_A$ is the charge on the atom A, on which the atomic orbital $\phi_\mu$ is centred, $q_v$ is the charge on the orbital $\phi_v$ centred on the atom B, defined as in (10)

TABLE 1

Parameters (in eV) used in the iterative extended-Hückel calculations (including Madelung corrections) for $[Cr_2O_{10}]^{14-}$ and $[Cr_2Cl_9]^{3-}$

| | | $A_\mu$ | $B_\mu$ | $C_\mu$ | $g_{\mu\mu}$ |
|---|---|---|---|---|---|
| Cr | 4*s* | 0.998<br>0.998<br>0.998 | 7.135<br>8.288<br>7.494 | 6.59<br>7.85<br>9.26 | 5.8 |
| | 4*p* | 0.899<br>0.899<br>0.899 | 5.895<br>6.552<br>6.552 | 3.52<br>4.69<br>4.72 | 4.3 |
| | 3*d* | 1.829<br>1.210<br>1.210 | 9.267<br>11.90<br>12.02 | 4.35<br>7.18<br>8.39 | 9.3 |
| O | 2*s* | | 15.2 | 33.00 | 15.2 |
| | 2*p* | | 15.2 | 16.40 | 15.2 |
| Cl | 3*s* | | 10.66 | 25.93 | 10.7 |
| | 3*p* | | 10.66 | 13.82 | 10.7 |

$$H_{\mu\mu} = -C_\mu - B_\mu q_A - A_\mu q_A^2 - \sum_{B \neq A} \sum_v q_v g_{\mu v} \qquad (9)$$

$$q_v = P_v^0 - P_v \qquad (10)$$

where $P_v^0$ and $P_v$ are the populations of $\phi_v$ in the complex deduced from Mulliken's analysis and that in the neutral atom respectively, and $g_{\mu v}$ is the two-centre electron-repulsion parameter defined as in (11). The parameters

$$g_{\mu v} = \left[ R_{AB}^2 + \left( \frac{g_{\mu\mu} + g_{vv}}{2 g_{\mu\mu} g_{vv}} \right)^2 \right]^{-\frac{1}{2}} \qquad (11)$$

$A_\mu$, $B_\mu$, $C_\mu$, and $g_{\mu\mu}$, taken from the program ICON (version 8) written by Hoffmann and his co-workers, are given in Table 1. For chromium 3*d*, 4*s*, and 4*p* orbitals, nine *A*, *B*, and *C* parameters instead of three are used, according to the equation of Ballhausen and Gray.[5]

The off-diagonal matrix element $H_{\mu v}$ is expressed by (12) and (13) where $S_{\mu v}$ is the overlap integral between $\phi_\mu$ and $\phi_v$, *q* is the total charge on the complex, and *N* is the number of valence electrons. The atomic orbitals used are simple Slater-type orbitals, except for chromium 3*d* orbitals for which we chose two-component orbitals: 2*s* and 2*p* exponents for oxygen are chosen using Slater's rules; 4*s* and 4*p* exponents for chromium come from Burns,[6] assuming a charge of +1 on the transition ion in the complexes. Finally, exponents and relative weights for chromium 3*d* orbitals were taken from Richardson *et al.*[7]

$$H_{\mu v} = \frac{K}{2} S_{\mu v} (H_{\mu\mu} + H_{vv}) + \left( \frac{1-K}{2} \right) S_{\mu v} (\Delta G_{\mu\mu} + \Delta G_{vv}) \qquad (12)$$

$$\Delta G_{\mu\mu} = -\frac{q}{N} \sum_v P_v g_{\mu v} \qquad (13)$$

The geometry of $[Cr_2O_{10}]^{14-}$ used for the calculation was idealized with regard to the actual geometry in order to have $C_2$ site symmetry for each chromium(III) ion and $D_{2h}$ symmetry for the binuclear complex. However, the average values of the angles were respected. These values are given in Figure 2.

We calculated the electronic structure of the hypothetical monomeric complex $[CrO_6]^{9-}$ and of the binuclear complex $[Cr_2O_{10}]^{14-}$. In both cases, the calculation was carried out for the electronic configuration in which the metal $e_g$ electrons are unpaired. This corresponds to the ${}^4B_1$ $[(a_1)^1(a_2)^1(b_2)^1]$ term for $[CrO_6]^{9-}$ and to the ${}^7B_{3u}$ $[(a_u)^1(b_{1u})^1(a_g)^1(b_{3g})^1(b_{2u})^1(b_{1g})^1]$ term for $[Cr_2O_{10}]^{14-}$. It is very important to understand that the energy gaps which occur in relation (3) must be calculated for the thermally accessible term of highest spin multiplicity. Only for this term are H.L. and m.o. wavefunctions identical.

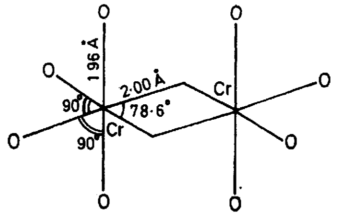

FIGURE 2 Geometry of $[Cr_2O_{10}]^{14-}$ used in the m.o. calculation

The parameter *K* of relation (12) was taken as 1.42. It was adjusted in order to lead to an energy of 18 000 cm⁻¹ for the ${}^4T_{2g}(t_{2g}{}^2e_g) \leftarrow {}^4A_{2g}(t_{2g}{}^3)$ transition. This transition is that observed in the spectrum of ruby in which the chromium(III) ion is in the same environment of six $O^{2-}$ ions.[8]

The energies of the singly occupied metal orbitals of $[CrO_6]^{9-}$ and $[Cr_2O_{10}]^{14-}$ are given in Table 2. These were corrected for the average value over all the valence orbitals of $\Delta G_{\mu\mu}$. This takes account of the electrostatic field arising from the crystal lattice. The $a_g$–$b_{1u}$, $b_{1g}$–$a_u$, and $b_{3g}$–$b_{2u}$ sets of m.o.s built from the $a_1$, $a_2$, and $b_2$ magnetic orbitals are schematized in Figure 3.

The overlap integrals $S_i$ may be approximated by applying equation (12) to the magnetic orbitals. This approximation is consistent with the use of the extended-Hückel method to determine the energies of the m.o.s.

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[4] J. R. Beswick and D. E. Dugdale, *Solid State Phys.*, 1973, **C6**, 3326.

[5] C. J. Ballhausen and H. B. Gray, ' Molecular Orbital Theory,' W. A. Benjamin, New York, 1964, p. 425.

[6] G. Burns, *J. Chem. Phys.*, 1964, **41**, 1521.

[7] J. W. Richardson, W. C. Nieuwport, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, 1962, **36**, 1057.

[8] D. L. Wood, J. Ferguson, K. Knox, and D. F. Dillon, jun., *J. Chem. Phys.*, 1963, **39**, 890.

Thus we have (14) where $\varepsilon_i$ is the one-electron energy for the magnetic orbital $\phi_{Ai}$ (or $\phi_{Bi}$). Neglecting $S_i^2$ compared to unity, (3) becomes (15). Taking again a $K$ value of 1.42 in (15), we find that $J_{AF}([Cr_2O_{10}]^{14-}) = -13$ cm$^{-1}$.

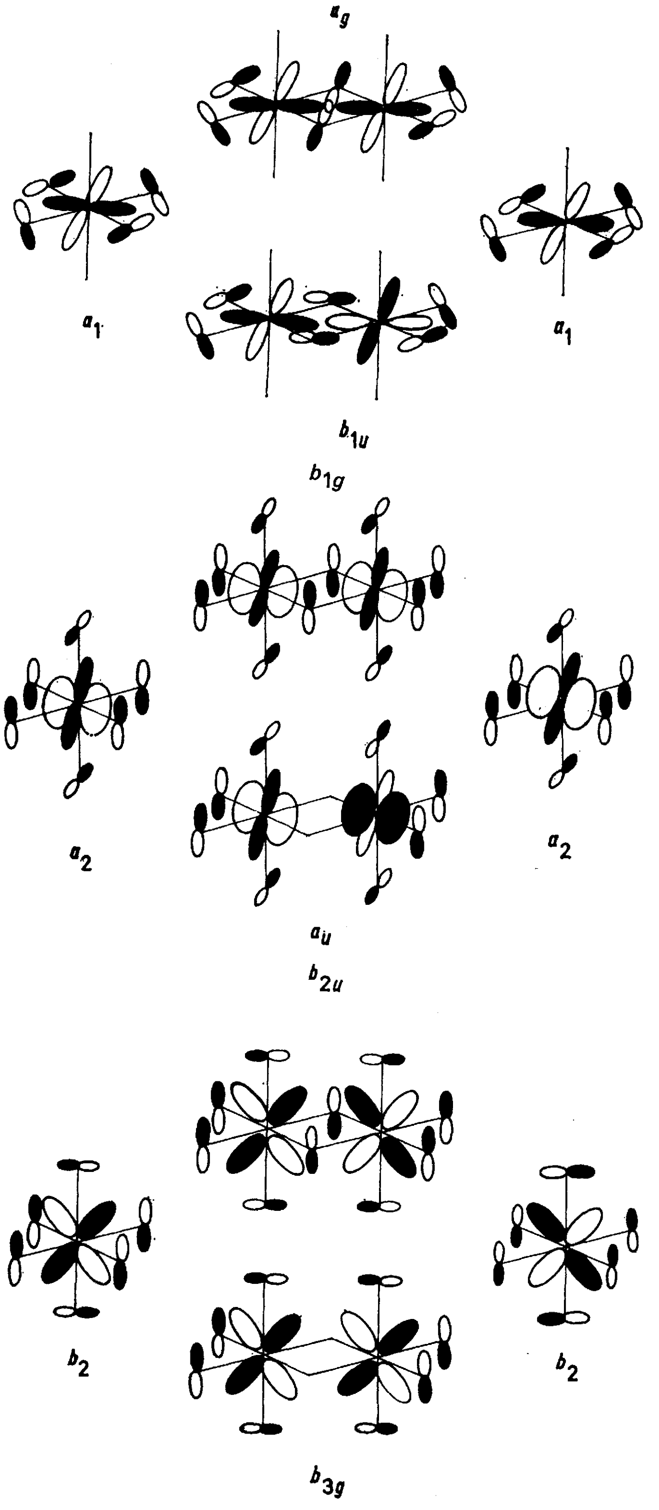

FIGURE 3 Schematic representation of the magnetic orbitals and of the m.o.s built from these magnetic orbitals in $[Cr_2O_{10}]^{14-}$

We made exactly the same calculation for $[Cr_2Cl_9]^{3-}$. The crystal structure of $Cs_3[Cr_2Cl_9]$ was determined by Wessel and Ijdo [9] and the exchange parameter by two of us (O. K. and B. B.).[10] $J$ is equal to $-13 \pm 1$ cm$^{-1}$.

$$S_i = -\frac{\Delta}{2(K-1)\varepsilon_i}(1 - S_i^2) \qquad (14)$$

$$J_{AF} = \frac{1}{(K-1)n^2}\sum_{i=1}^{n}\frac{\Delta_i^2}{\varepsilon_i} \qquad (15)$$

The $A_\mu$, $B_\mu$, $C_\mu$, and $g_{\mu\mu}$ parameters for the chlorine $3s$ and $3p$ orbitals are given in Table 1 and the exponents of these orbitals were chosen from Slater's rules. The same $K$ parameter of 1.42 leads to the experimentally observed energy of 13 200 cm$^{-1}$ for the $^4T_{2g} \leftarrow {^4A_{2g}}$ transition in $Cs_3[CrCl_6]$.[11]

TABLE 2

Symmetries and energies (in eV) of the magnetic orbitals and of the m.o.s built from these magnetic orbitals for $[Cr_2Cl_{10}]^{14-}$

| | $[CrO_6]^{9-}$ | | $[Cr_2O_{10}]^{14-}$ |
|---|---|---|---|
| | | $b_{1g}$ | −13.893 46 |
| $b_2$ | −13.246 94 | $b_{2u}$ | −13.912 90 |
| | | $b_{3g}$ | −14.035 73 |
| $a_2$ | −13.292 06 | | |
| | | $a_g$ | −14.075 39 |
| $a_1$ | −13.299 45 | $b_{1u}$ | −14.083 86 |
| | | $a_u$ | −14.147 39 |

Table 3 contains the one-electron energies of the magnetic orbitals in $[CrCl_6]^{3-}$ and of the m.o.s built from these magnetic orbitals in $[Cr_2Cl_9]^{3-}$. From these energies, we find that $J_{AF}([Cr_2Cl_9]^{3-}) = -23$ cm$^{-1}$.

TABLE 3

Symmetries and energies (in eV) of magnetic orbitals and of the m.o.s built from these magnetic orbitals for $[Cr_2Cl_9]^{3-}$

| | $[CrCl_6]^{3-}$ | | $[Cr_2Cl_9]^{3-}$ |
|---|---|---|---|
| $a_1$ | −12.701 86 | $a_2''$ | −12.671 28 |
| | | $e'$ | −12.847 84 |
| $e$ | −12.717 97 | $e''$ | −12.921 36 |
| | | $a_1'$ | −13.027 52 |

## CONCLUSIONS

In our approach, as in those previously proposed, the experimentally observed $J$ parameter, whatever its sign may be, is interpreted as resulting from an antiferromagnetic component $J_{AF}$ and from a ferromagnetic component $J_F$. The basic hypothesis of this work is that the variation in $J_{AF}$ is a good indication of that in $J$ for similar compounds in which the transition ions are antiferromagnetically coupled. This is equivalent to assuming either that $J_F$ is always very small, or that $J_{AF}/J_F$ is constant for similar compounds.

For neither of the complexes $[Cr_2O_{10}]^{14-}$ and $[Cr_2Cl_9]^{3-}$ did we calculate the ferromagnetic contribution $J_F$ given

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[9] G. J. Wessel and D. J. W. Ijdo, *Acta Cryst.*, 1957, **10**, 466.

[10] O. Kahn and B. Briat, *Chem. Phys. Letters*, 1975, **32**, 376.

[11] B. Briat, M. F. Russel, J. C. Rivoal, J. P. Chapelle, and O. Kahn, *Mol. Phys.*, in the press.

by (16), where the indices $i$ and $j$ extend over all the magnetic orbitals. The rather poor quality of the orbital-basis functions would make such a calculation

$$J_F = \frac{2}{9} \sum_{i=1}^{3} \sum_{j=1}^{3} J_{ij} \qquad (16)$$

only weakly credible. Focusing on $J_{AF}$, we see that our model leads to good orders of magnitude and good relative values of the exchange interaction. A higher accuracy may not be expected considering the method of calculation and the choice of the basis set. It would be particularly interesting to apply our model in the framework of an *ab initio* calculation. Even for the simplest binuclear transition-metal system, such an *ab initio* calculation is not yet tractable. The difficulty arises not only from the size of the chemical system but also from the necessity to perform an open-shell calculation. Indeed, we recall that the $\Delta_i$ energy gaps in relation (3) must be obtained from the low-lying term of highest spin multiplicity.

The main purpose of this work is the interpretation and eventually the prediction of the order of magnitude of the $J$ parameter characterizing the exchange phenomenon. In case of antiferromagnetic coupling, we think the model used in this paper permits such an interpretation. On the other hand, in the few cases where the coupling appears to be ferromagnetic, both experimental and theoretical studies are necessary.

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